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Resolution of phase ambiguities in electron-impact ionization amplitudes

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The formal theory of atomic ionization by electron impact relates the breakup amplitude to an integral expression involving the exact wave function and an unperturbed final state that contains two Coulomb functions with effective, noninteger charges. This integral expression has an associated phase factor that diverges logarithmically on an infinite volume unless the effective charges are chosen to satisfy a kinematic relationship, the so-called ''Peterkop condition.'' We derive the explicit form of the Peterkop phase for two commonly used models of electron-hydrogen ionization, the Temkin-Poet model and the collinear model. We show that the formal theory can be used to identify and remove this physically insignificant, volume-dependent phase from amplitudes computed using numerically stable integral expressions that do not satisfy the Peterkop condition.

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There are a variety of theoretical techniques capable of producing accurate total electron-impact ionization cross sections, even at collision energies close to threshold. The accurate prediction of differential ionization cross sections is another matter entirely and to date only a few methods have produced stable differential ionization cross sections at low impact energies over the entire range of available energy sharing. The method of exterior complex scaling (ECS) is one such method and relies on a (complex) scaling of the radial electron coordinates outside a (hyper)sphere of finite volume to obviate the need for explicit imposition of three-body asymptotic boundary conditions in computing the scattering wave function [1]. Early implementations of the method [2] relied on a direct evaluation of the quantum-mechanical flux through a finite hypersurface, followed by numerical extrapolation to infinite volume to obtain physical cross sections. We have since developed more efficient methods based on integral expressions for the scattering amplitude [3].

The use of integral expressions for the ionization amplitude in numerical calculations raises some interesting formal questions. In the formal theory developed some 40 years ago, Peterkop [4] and Rudge and Seaton [5] considered the question of how to define the breakup amplitude in terms of an integral of the form

$$I = \int \Psi(\mathbf{r}_1,\mathbf{r}_2)(H-E)\Psi_0(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2, \qquad (1)$$

where Ψ_0 is a reference function corresponding to the final state with two electrons in the continuum, whose form the formal theory seeks to define, and Ψ is the full solution of the Schrödinger equation satisfying the correct boundary conditions for ionization. These authors pointed out that if the final state is represented as a product of Coulomb waves, $\Psi_0 = \phi_{-\mathbf{k}_1}(\mathbf{r}_1;z_1)\phi_{-\mathbf{k}_2}(\mathbf{r}_2;z_2)$, then this integral is related to the breakup amplitude, $f(\mathbf{k}_1,\mathbf{k}_2)$, by

$$I \propto f(\mathbf{k}_1,\mathbf{k}_2) \lim_{\rho\to\infty} \exp\{i\mathfrak{F}(z_1,\mathbf{k}_1;z_2,\mathbf{k}_2)\ln(2K\rho)\}, \qquad (2)$$

where ρ is the hyperradius defining the volume of integration.

The main point is that the integral in Eq. (1) is proportional to the breakup amplitude, but with a volume-dependent overall ''Peterkop phase,'' *unless* the charges, z_1 and z_2, associated with the two Coulomb functions satisfy the dynamical ''Peterkop condition'' $\mathfrak{F}(z_1,\mathbf{k}_1;z_2,\mathbf{k}_2)=0$ (which we discuss in detail below). The phase in question is an overall phase in the amplitude for a specific physical process, and as such does not change any physical observable.

However, for numerical calculations carried out over a finite volume, we have shown that the use of effective charges other than 1 leads to serious numerical problems, because only Coulomb functions with $z=1$ are orthogonal to the bound states of the target atom [6]. On a finite volume, there are of course no problems with divergent phase factors, but one might naturally be led to question whether amplitudes calculated with Coulomb functions that do not satisfy the Peterkop condition give physically correct cross sections. We have addressed this point in several earlier papers [6,7] and shown it to be inconsequential [3]. Nevertheless, the issue of calculating the correct phase has recently been raised [8], prompting us to examine this subject in more detail.

We show below that the logarithmic component of the phase in Eq. (2) is entirely predictable and can be removed from the computed amplitude, so long as the volume of the integration in Eq. (1) is well defined. We emphasize that it is not necessary to remove this phase in any practical calculation. The only interest in doing so is to compare the results of different computational methods. No currently known physical observable can depend on it.

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To illustrate our discussion, we use two popular two-dimensional models of electron-hydrogen ionization: the Temkin-Poet, or *S*-wave, model and the collinear model. The first step is to establish the asymptotic form of the scattering wave function with two electrons in the continuum. The radial Schrödinger equation for a two-electron problem with no angular momentum is

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial r_1^2}-\frac{1}{2}\frac{\partial^2}{\partial r_2^2}+V(r_1,r_2)\right]\Psi=E\Psi, \tag{3}$$

where $E=K^2/2$ is the total energy and $V(r_1,r_2)$ is the full interaction potential,

$$V(r_1,r_2)=-\frac{1}{r_1}-\frac{1}{r_2}+V_2. \tag{4}$$

and V_2 is the (model) two-body interaction. In hyperspherical coordinates $[\rho=\sqrt{r_1^2+r_2^2},\ \tan(\alpha)=r_2/r_1]$, Eq. (3) becomes, with $\Psi=\Phi/\rho^{1/2}$,

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial\rho^2}-\frac{1}{8\rho^2}-\frac{1}{2\rho^2}\frac{\partial^2}{\partial\alpha^2}-\frac{\zeta(\alpha)}{\rho}\right]\Phi=E\Phi, \tag{5}$$

where the interaction potential has been rewritten as

$$V(r_1,r_2)=-\frac{\zeta(\alpha)}{\rho}. \tag{6}$$

Following Rudge's approach [9] for the full ionization problem, we rearrange the Schrödinger equation as

$$\left[\frac{K^2}{2}+\frac{1}{2}\frac{\partial^2}{\partial\rho^2}+\frac{1}{8\rho^2}+\frac{\zeta(\alpha)}{\rho}\right]\Phi=-\frac{1}{2\rho^2}\frac{\partial^2}{\partial\alpha^2}\Phi, \tag{7}$$

and formally solve this using the Coulomb Green's function with α as a parameter on the left-hand side. The Green's function $G(\rho,\rho')$ is expressed in terms of regular and outgoing functions F and H with asymptotic forms

$$F(\zeta,K,\rho)\sim\sin[f(\rho)],\quad \rho\to\infty,$$
$$H(\zeta,K,\rho)\sim\exp[if(\rho)],\quad \rho\to\infty \tag{8}$$

and

$$f(\rho)=K\rho+\frac{\zeta}{K}\ln(2K\rho)+\frac{\pi}{4}+\arg\Gamma\left(\frac{1}{2}-i\frac{\zeta}{K}\right) \tag{9}$$

as

$$G(\rho,\rho')=-\frac{2}{K}F(\zeta,K,\rho_<)H(\zeta,K,\rho_>), \tag{10}$$

and satisfies the equation

$$\left[\frac{K^2}{2}+\frac{1}{2}\frac{\partial^2}{\partial\rho^2}+\frac{1}{8\rho^2}+\frac{\zeta(\alpha)}{\rho}\right]G(\rho,\rho')=\delta(\rho-\rho'). \tag{11}$$

It immediately follows that the asymptotic form of the wave function can be written as

$$\Psi(r_1,r_2)=-\frac{1}{\sqrt{\rho}}\int_0^\infty d\rho' G(\rho,\rho')\frac{1}{2\rho'^2}\frac{\partial^2}{\partial\alpha^2}\Phi(\rho',\alpha)$$
$$\underset{\rho\to\infty}{\sim}\frac{A(\alpha)}{\sqrt{\rho}}\exp\left[i\left(K\rho+\frac{\zeta(\alpha)}{K}\ln(2K\rho)\right)\right], \tag{12}$$

with the ionization amplitude $A(\alpha)$ identified as

$$A(\alpha)=\frac{1}{K}\exp\left\{i\left[\frac{\pi}{4}+\arg\Gamma\left(\frac{1}{2}-i\frac{\zeta(\alpha)}{K}\right)\right]\right\}$$
$$\times\int_0^\infty d\rho F(\zeta,K,\rho)\frac{1}{2\rho^2}\frac{\partial^2}{\partial\alpha^2}\Phi(\rho,\alpha). \tag{13}$$

A knowledge of the asymptotic form of the wave function is all that is required to develop integral expressions for the scattering amplitude. We again follow the course outlined by Peterkop [4] and by Rudge and Seaton [5] and consider the integral in Eq. (1) for two radial variables. To evaluate the integral I in this case we again switch to hyperspherical coordinates and use Green's theorem to express it as a surface integral:

$$I=-\frac{1}{2}\lim_{\rho\to\infty}\int_0^{\pi/2}\left[\Psi\frac{\partial\Psi_0}{\partial\rho}-\Psi_0\frac{\partial\Psi}{\partial\rho}\right]\rho d\alpha. \tag{14}$$

We now choose Ψ_0 to be the product of two radial Coulomb functions with effective charges z_1 and z_2 and momenta k_1 and k_2 defined as

$$k_1=K\cos(\beta),$$
$$k_2=K\sin(\beta). \tag{15}$$

With these definitions, we have

$$\Psi_0(r_1,r_2)=\phi_{k_1}(r_1;z_1)\phi_{k_2}(r_2;z_2), \tag{16}$$
$$\phi_k(r;z)\sim\sin\left(kr+\frac{z}{k}\ln(2kr)+\sigma_k(z)\right),\quad r\to\infty,$$

where

$$\sigma_k(z)=\arg\Gamma\left(1-i\frac{z}{k}\right). \tag{17}$$

After substituting the asymptotic forms given in Eqs. (12) and (16) into Eq. (14), we can express the integral as

$$I=\frac{1}{2}\lim_{\rho\to\infty}\frac{e^{iK\rho}}{\sqrt{\rho}}\int_0^{\pi/2}d\alpha A(\alpha)e^{i[K\rho+\zeta(\alpha)/K\ln(2K\rho)]}\left[\frac{i\zeta(\alpha)}{k\rho}-\frac{\partial}{\partial\rho}\right.$$
$$\left.-\frac{1}{2\rho}\right]\left[\sin\left(k_1\rho\cos\alpha+\frac{z_1}{k_1}\ln(2k_1\rho\cos\alpha)+\sigma_{k_1}(z_1)\right)\right]$$
$$\times\left[\sin\left(k_2\rho\cos\alpha+\frac{z_2}{k_2}\ln(2k_2\rho\cos\alpha)+\sigma_{k_2}(z_2)\right)\right]. \tag{18}$$

The integration can be carried out using the method of stationary phase [10], which is exact in the limit $\rho\to\infty$. The algebra is tedious, but straightforward, and will not be reproduced here. The key identity needed in the derivation is the stationary phase result:

$$\int_0^{\pi/2} f(\alpha)\sin[k_1\rho\cos(\alpha)+g(\alpha)]\sin[k_2\rho\sin(\alpha)+h(\alpha)]$$

$$\underset{\rho\to\infty}{\sim} -\frac{1}{2}f(\alpha_0)\sqrt{\frac{2\pi}{K\rho}}\cos\left(K\rho+g(\alpha_0)\right.$$

$$\left.+h(\alpha_0)-\frac{\pi}{4}\right), \tag{19}$$

where the stationary point α_0 is given by the condition $\tan\alpha_0=k_2/k_1$ or, in view of Eq. (15), $\alpha_0=\beta$. It is then possible, by performing the integral over α in Eq. (18) before differentiating with respect to ρ, to derive the desired result

$$I \underset{\lim\rho\to\infty}{=} -\frac{1}{4}\sqrt{2\pi K}iA(\beta)\exp\left[-i\left(Q(k_1,z_1)+Q(k_2,z_2)\right.\right.$$

$$\left.\left.+\frac{3\pi}{4}\right)\right]\exp\left[i\left(\frac{\zeta(\beta)}{K}-\frac{z_1}{k_1}-\frac{z_2}{k_2}\right)\ln(2K\rho)\right]+O(1/\rho), \tag{20}$$

with

$$Q(k;z)=\sigma_k(z)+2\frac{z}{k}\ln(k/K). \tag{21}$$

The integral defined by Eq. (1) is thus proportional to the physical breakup amplitude times a logarithmic phase factor, which diverges in the limit $\rho\to\infty$, unless the effective charges are chosen to satisfy the condition [4]

$$\frac{\zeta(\beta)}{K}=\frac{z_1}{k_1}+\frac{z_2}{k_2}. \tag{22}$$

On any finite volume, the "Peterkop phase," $\phi\equiv(\zeta(\beta)/K-z_1/k_1-z_2/k_2)\ln(2K\rho)$, is well defined.

We now turn to the two models previously mentioned. In the Temkin-Poet model, the full interaction potential is replaced by its spherical average, $V(r_1,r_2)=-1/r_1-1/r_2+1/r_>=-1/r_<$ which, according to Eqs. (6) and (20), defines the Peterkop phase as

$$\phi_{TP}=\left(\frac{1}{k_<}-\frac{z_1}{k_1}-\frac{z_2}{k_2}\right)\ln(2K\rho). \tag{23}$$

Not surprisingly, the choice $z_1=0$ and $z_2=1$ makes the phase vanish for all $k_1\geqslant k_2$. In the Temkin-Poet model, the separable nature of the potential leads to a complete screening of the fast electron by the slow electron, so that the product of a free function and a Coulomb function is the "correct" final state in this case, and provides the proper boundary condition for an exact numerical treatment [11]. This fact is peculiar to the Temkin-Poet case, however, and does not extend to other two-dimensional (2D) models, nor to the full problem. In our previous work on calulating ionization amplitudes, we showed that it is essential to maintain orthogonality between the Coulomb distorted waves and the bound hydrogenic states and therefore remove any spurious contributions to the breakup amplitude that arise from discrete two-body excitation channels. This leads naturally to the choice $z_1=z_2=1$, as explained at length in Refs. [7] and [6]. The choice $z_1=z_2=1$ gives a Peterkop phase of $-1/k_>\ln(2K\rho)$.

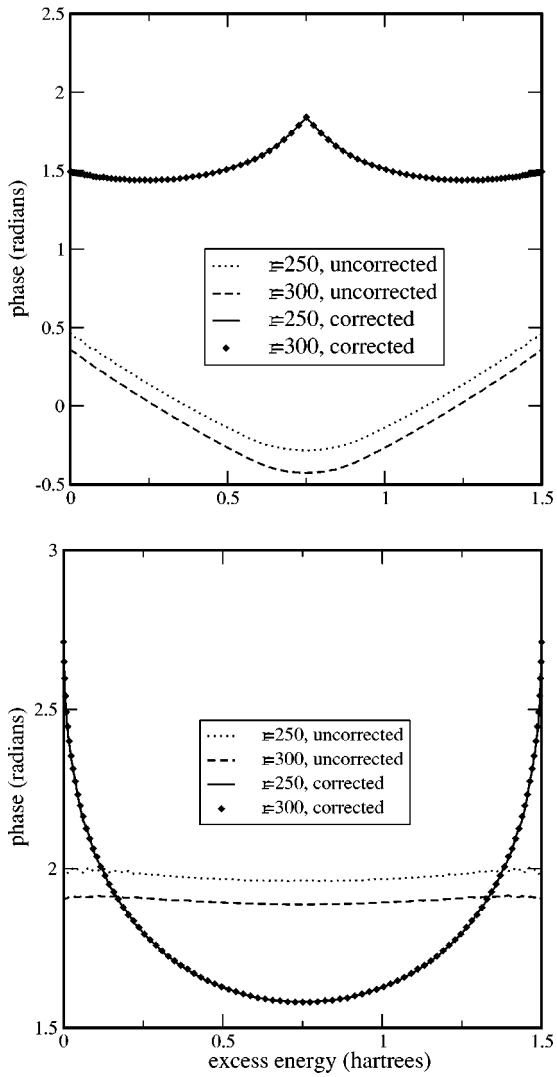

FIG. 1. Phase of the computed amplitude for the singly differential cross section for breakup at a total energy of 1.5 hartrees for different 2D models of *e*-H ionization. Upper panel, Temkin-Poet model; lower panel, collinear model. The curves labeled uncorrected were computed using Eq. (14) at a fixed value of the hyperradius. The corrected curves are obtained by removing the appropriate volume dependent portions of the phase for each model, as discussed in the text.

The collinear model uses $V(r_1,r_2)=-1/r_1-1/r_2+1/(r_1+r_2)$. In that case, the Peterkop phase is

$$\phi_{col}=\frac{1}{K}\left[\frac{(1-z_1)}{\cos(\beta)}+\frac{(1-z_2)}{\sin(\beta)}-\frac{1}{[\cos(\beta)+\sin(\beta)]}\right]\ln(2K\rho). \tag{24}$$

For this case, there is no β-independent choice of effective

charges that can lead to a vanishing phase. The ECS choice $z_1=z_2=1$ gives a phase of $-1/(k_1+k_2)\ln(2K\rho)$.

We now turn to some numerical demonstrations. We carried out ECS calculations of *e*-H ionization for the singlet spin case at a total energy of 1.5 hartree for both the Temkin-Poet and collinear models. The scattered wave functions were generated on a two-dimensional square grid the real portion of which extended to 300 Bohr in r_1 and r_2. We used the finite-element/discrete variable representation previously described [12] to solve the 2D Schrödinger equation. The ionization amplitude was computed at a fixed value of the hyperradius, using Eq. (14), and two Coulomb functions with $z=1$ in the final state. The surface integrals were evaluated at hyperradii of 250 and 300 bohrs. The resulting phases, as a function of ejected electron energy, are shown in Fig. 1. For the Temkin-Poet case, shown in the upper panel of Fig. 1, the phase of the computed amplitude is seen to depend on hyperradius. By adding $1/k_>\ln(2K\rho)$ to the computed phase, we produce a result that is independent of ρ to the numerical accuracy of the calculations. By further adding $Q(k_>,1)$ we produce the phase that is plotted, which should correspond to the phase one would obtain in an exact numerical integration of the Temkin-Poet model [11]. The results for the collinear case are shown in the lower panel of Fig. 1. In this case, addition of $1/(k_1+k_2)\ln(2K\rho)$ to the computed phase again produces a ρ-independent result.

So what have we learned from this exercise? We have shown that for any 2D model of electron impact ionization, the breakup amplitude, computed from a numerically generated wave function on a finite hypersphere, will have a phase component, which we have called the ''Peterkop phase,'' that depends logarithmically on the hyperradius. For any 2D model, this phase, which can depend only on the hyperangle β, can easily be predicted, calculated and, if desired, removed from the total phase. For the full six-dimensional problem, the Peterkop phase, which is given by

$$\left[\frac{1}{k_1}+\frac{1}{k_2}-\frac{1}{|\mathbf{k}_1-\mathbf{k}_2|}-\frac{z_1}{k_1}-\frac{z_2}{k_2}\right]\ln(2K\rho), \qquad (25)$$

depends on the speed and direction of ejection of both electrons and can, in principle, be removed, but not so easily as in the models considered here. Most approaches, including ECS, use a partial-wave decomposition of the full wave function and the various numerically computed L components are combined coherently to produce the total ionization amplitude. This construction effectively includes the Peterkop phase if the various pieces are all computed with the same hyperradius. This is an essential point, since an inconsistent choice of hyperradii would produce phase inconsistencies between the various partial-wave components of the amplitude and, consequently, incorrect doubly or triply differential cross sections. When the Peterkop phase is correctly constructed, it factors out of the total amplitude and makes no contribution to any observable cross section [3].

We have also shown that the choice $z_1=0$, $z_2=1$, which is used in most basis-set close-coupling approaches, only eliminates the Peterkop phase in the special case of the Temkin-Poet model. For the full problem, this would not be the case. Moreover, since there is really no well-defined hypersphere in such approaches, apart from the ''volume'' defined by the range of the basis sets employed, it would seem that the task of maintaining phase consistency between the various partial-wave amplitudes is not as straightforward. Indeed, recently published work on triply differential ionization cross sections for *e*-H using the convergent close-coupling method [13] has stressed the importance of using a single basis-set scaling parameter (orbital exponent) for all partial waves to avoid apparent convergence to an incorrect result. Since this parameter controls the range of the basis, we can only speculate that this finding reflects the necessity of maintaining a consistent phase convention between the various partial-wave components of the amplitude.

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